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(54) OPTICAL SEMICONDUCTOR ELECTRODEPHOTOELECTRIC CONVERTER AND PHOTOELECTRIC CONVERSION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To efficiently utilize sunlight by providing a photoelectric conversion layer of one kind or more of a tetracyanoanthraquinodimethan compound and a perylene compound on the surface of a metal oxide semiconductor.

SOLUTION: This tetracyanoanthraquinodimethan compound is shown in a formula I. In the formula I R1 and R2 are a hydrogen atomalkyl grouparyl groupalkyl groupalkoxyalkyl group or acyl group; n is 0 or 1. This perylene compound is shown in a formula II. In the formula II R3 and R4 are a group represented by a formula III etc.; when the R3 and R4 are a group represented by the formula IIII is 0. In the formula IIIR5 and R6 are an aliphatic grouparomatic group or heterocyclic group; these may be substituted by a substituent. A1 represents a bivalent aliphatic grouparomatic group or heterocyclic group; these may be substituted by a substituent.

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### CLAIMS

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[Claim(s)]

[Claim 1]An optical semiconductor electrode having a photoelectric

conversion layer by at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) on the surface of a metal oxide semiconductor.

General formula (I)

[Formula 1]

In said general formula (I)  $R^1$  and  $R^2$  It may be mutually the same and may differ a hydrogen atom an alkyl group an aryl group an aralkyl group an alkoxyalkyl group or an acyl group may be expressed and these may form the annular group of the following structure mutually. n expresses 0 or 1.

[Formula 2]

General formula (II)

[Formula 3]

In said general formula (II)  $R^3$  and  $R^4$  Expressing the basis expressed with either following general formula (III) - (IX) these may be mutually the same it may differ and at least one side expresses the basis expressed with either following general formula (III) - (VII) and (IX). 1 expresses 0-12 when it is a basis which expresses 0 when  $R^3$  and  $R^4$  are the bases expressed with either following general formula (III) - (VIII) and is expressed with following general formula (IX).

General formula (III)

[Formula 4]

In said general formula (III)  $R^5$  and  $R^6$  may be mutually the same it may differ an aliphatic group an aromatic group or a heterocycle group is expressed and these may be replaced by the substituent.  $A^1$  expresses a divalent aliphatic group aromatic group or heterocycle group and these may be replaced by the substituent.

General formula (IV)

[Formula 5]

In said general formula (IV)  $A^2$  expresses a divalent aliphatic group aromatic group or heterocycle group and these may be replaced by the

substituent.  $R^7$  and  $R^8$  may be mutually the same and it may differ. A hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-20- $(CH_2)_pCOOR^{18}$ -( $CH_2$ ) $_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$  is expressed.  $R^{18}R^{19}R^{20}$  and  $R^{21}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (V)

[Formula 6]

In said general formula (V)  $A^3$  expresses a single bond or a divalent aliphatic group, an aromatic group or a heterocycle group and these may be replaced by the substituent.  $R^9$  expresses an aliphatic group, an aromatic group or a heterocycle group and these may be replaced by the substituent.  $R^{10}$  A hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-20- $(CH_2)$  Express  $_pCOOR^{18}$ -( $CH_2$ ) $_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}R^{19}R^{20}$  and  $R^{21}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (VI)

[Formula 7]

In said general formula (VI)  $A^4$  expresses a divalent aliphatic group, an aromatic group or a heterocycle group and these may be replaced by the substituent.  $X$  expresses an oxygen atom, a sulfur atom or  $>NR^{22}$ .  $R^{11}$  and  $R^{12}$  A hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-20- $(CH_2)$  Express  $_pCOOR^{18}$ -( $CH_2$ ) $_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}R^{19}R^{20}R^{21}$  and  $R^{22}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (VII)

[Formula 8]

In said general formula (VII)  $A^5$  expresses a single bond or a divalent aliphatic group, an aromatic group or a heterocycle group and these may be replaced by the substituent.  $R^{13}$  expresses a divalent aliphatic group, an aromatic group or a heterocycle group and these may be replaced by the substituent.  $R^{14}$  A hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-20- $(CH_2)$  Express  $_pCOOR^{18}$ -( $CH_2$ ) $_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}R^{19}R^{20}$  and  $R^{21}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (VIII)

[Formula 9]

In said general formula (VIII) A<sup>6</sup> expresses a divalent aliphatic group, aromatic group or heterocycle group and these may be replaced by the substituent. Y expresses -COOH-SO<sub>3</sub>H or -NH<sub>2</sub>.

General formula (IX)

[Formula 10]

In said general formula (IX) X expresses two hydrogen atoms or Mg, Zn, Fe, Co, Ni, Cu, Ru, Sn, Ti, V, O, Al, Ga, In, OH. R<sup>15</sup>, R<sup>16</sup> and R<sup>17</sup> express a hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-12, -(CH<sub>2</sub>)<sub>m</sub>-COOH or -(CH<sub>2</sub>)<sub>m</sub>-NH<sub>2</sub>. m and n express the integer of 0-12.

[Claim 2] The optical semiconductor electrode according to claim 1 whose tetracyanoanthraquinodimethane compound expressed with said general formula (I) is a tetracyanoanthraquinodimethane compound expressed with a following general formula (I-a).

A general formula (I-a)

[Formula 11]

In said general formula (I-a) Me expresses a methyl group. n expresses 0 or 1.

[Claim 3] The optical semiconductor electrode according to claim 1 or 2 whose metal oxide semiconductor is at least one sort chosen from titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, nickel oxide, cobalt oxide and strontium titanate.

[Claim 4] A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple contacted to an electrolyte and an electrode of this couple so that energization is possible and is characterized by at least one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 3.

[Claim 5] It is the photoelectric conversion method of contacting an electrode of a couple mutually connected so that energization was possible to an electrolyte and producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. A photoelectric conversion method that an electrode with which light is irradiated is characterized by being the optical semiconductor

electrode according to any one of claims 1 to 3.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optical semiconductor electrode to which the specific compound was made to stick on the surface of a metal oxide semiconductor the photoelectric conversion device using it and the photoelectric conversion method.

[0002]

[Description of the Prior Art] In recent years use of sunlight attracts attention as an energy resource replaced with fossil fuel such as petroleum and coal. As a device which transforms light energy into electrical energy directly the dry type solar cell in which pn junction was formed on inorganic semiconductor such as silicon and gallium arsenide is known well and it is put in practical use as a power supply of the object for remote places or a portable electronic device etc.

However conversion efficiency with these expensive solar cells is acquired.

On the other hand since the energy and cost which manufacture takes are very high there is a problem that it is difficult to use as an energy resource.

[0003] The wet solar cell which on the other hand used the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as an option which transforms light energy into electrical energy is known. As compared with the above-mentioned silicon gallium arsenide etc. metal oxide semiconductors used here such as titanium oxide tin oxide and a zinc oxide can be manufactured at far low energy and cost and are expected as a future energy conversion material. However since a stable metal oxide semiconductor like titanium oxide has the band gap as large as not less than 3 eV only about 4% of ultraviolet radiation of sunlight can be used and the way things stand high conversion efficiency cannot be expected. On the surface of these metal oxide semiconductors as sensitizing dye Thence cyanine dye and a xanthene dye organic coloring matter (H. -- Tsubomura et. al. Nature. 261 and 402 (1976).) such as coumarin coloring matter M. To make Matsumura et. al. Bull. Chem. Soc. Jpn. 502533 (1977) JP10-92477A JP10-93118A etc. adsorb and to carry out spectral sensitization is

tried. However when the above-mentioned cyanine dye, xanthene dye, coumarin coloring matter etc. are used there is a problem that photoelectric conversion efficiency is not enough.

[0004]

[Problem(s) to be Solved by the Invention] This invention solves many problems in said former and makes it a technical problem to attain the following purposes. That is, this invention can carry out available [ of the sunlight ] efficiently and is excellent in photoelectric conversion efficiency, stability, endurance etc. and an object of this invention is to provide the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency using the optical semiconductor electrode which can be manufactured cheaply and easily and this optical semiconductor electrode.

[0005]

[Means for Solving the Problem] Said The means for solving a technical problem is as follows. That is, it is an optical semiconductor electrode having a photoelectric conversion layer by at least one sort chosen as the surface of (1) metal oxide semiconductor from a perylene compound expressed with a tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I).

General formula (I)

[0006]

[Formula 12]

[0007] In said general formula (I)  $R^1$  and  $R^2$  It may be mutually the same and may differ, a hydrogen atom, an alkyl group, an aryl group, an alkyl group, an alkoxyalkyl group or an acyl group may be expressed and these may form the annular group of the following structure mutually. n expresses 0 or 1.

[0008]

[Formula 13]

[0009] General formula (II)

[Formula 14]

[0010] In said general formula (II)  $R^3$  and  $R^4$  Expressing the basis expressed with either following general formula (III) - (IX) these may be mutually the same, it may differ and at least one side expresses the basis

expressed with either following general formula (III) - (VII) and (IX).  
 1 expresses 0-12 when it is a basis which expresses 0 when  $R^3$  and  $R^4$  are  
 the bases expressed with either following general formula (III) -  
 (VIII) and is expressed with following general formula (IX).

General formula (III)

[0011]

[Formula 15]

[0012] In said general formula (III)  $R^5$  and  $R^6$  may be mutually the same it  
 may differ an aliphatic group an aromatic group or a heterocycle group is  
 expressed and these may be replaced by the substituent.  $A^1$  expresses a  
 divalent aliphatic group aromatic group or heterocycle group and these may  
 be replaced by the substituent.

General formula (IV)

[0013]

[Formula 16]

[0014] In said general formula (IV)  $A^2$  expresses a divalent aliphatic  
 group aromatic group or heterocycle group and these may be replaced by the  
 substituent.  $R^7$  and  $R^8$  may be mutually the same and it may differ a  
 hydrogen atom a halogen atom the alkyl group of the carbon numbers 1-20-  
 $(CH_2)_p COOR^{18} - (CH_2)_p SO_3R^{19}$  or  $-(CH_2)_p R^{20}R^{21}$  is expressed.  $R^{18}R^{19}R^{20}$  and  $R^{21}$   
 express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$   
 expresses the integer of 0-20.

General formula (V)

[0015]

[Formula 17]

[0016] In said general formula (V)  $A^3$  expresses a single bond or a  
 divalent aliphatic group an aromatic group or a heterocycle group and these  
 may be replaced by the substituent.  $R^9$  expresses an aliphatic group an  
 aromatic group or a heterocycle group and these may be replaced by the  
 substituent.  $R^{10}$  A hydrogen atom a halogen atom the alkyl group of the  
 carbon numbers 1-20-  $(CH_2)_p$  Express  $_p COOR^{18} - (CH_2)_p SO_3R^{19}$  or  $-(CH_2)_p NR^{20}R^{21}$ .  
 $R^{18}R^{19}R^{20}$  and  $R^{21}$  express the alkyl group of a hydrogen atom or the carbon  
 numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (VI)

[0017]

[Formula 18]

[0018] In said general formula (VI)  $A^4$  expresses a divalent aliphatic group, an aromatic group, or a heterocycle group, and these may be replaced by a substituent.  $X$  expresses an oxygen atom, a sulfur atom, or  $>NR^{22}$ .  $R^{11}$  and  $R^{12}$  are a hydrogen atom, a halogen atom, an alkyl group of the carbon numbers 1-20,  $-(CH_2)_p$ ,  $COOR^{18}$ ,  $-(CH_2)_pSO_3R^{19}$ , or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}$ ,  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$ , and  $R^{22}$  express an alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses an integer of 0-20.

General formula (VII)

[0019]

[Formula 19]

[0020] In said general formula (VII)  $A^5$  expresses a single bond or a divalent aliphatic group, an aromatic group, or a heterocycle group, and these may be replaced by a substituent.  $R^{13}$  expresses a divalent aliphatic group, an aromatic group, or a heterocycle group, and these may be replaced by a substituent.  $R^{14}$  is a hydrogen atom, a halogen atom, an alkyl group of the carbon numbers 1-20,  $-(CH_2)_p$ ,  $COOR^{18}$ ,  $-(CH_2)_pSO_3R^{19}$ , or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}$ ,  $R^{19}$ ,  $R^{20}$ , and  $R^{21}$  express an alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses an integer of 0-20.

General formula (VIII)

[0021]

[Formula 20]

[0022] In said general formula (VIII)  $A^6$  expresses a divalent aliphatic group, an aromatic group, or a heterocycle group, and these may be replaced by a substituent.  $Y$  expresses  $-COOH$ ,  $-SOOH$ , or  $-NH_2$ .

General formula (IX)

[0023]

[Formula 21]

[0024] In said general formula (IX)  $X$  expresses two hydrogen atoms or Mg, Zn, Fe, Co, Ni, Cu, Ru, Sn, Ti, V, O, aluminum, (OH), Ga, (OH), or In, (OH).  $R^{15}$ ,  $R^{16}$ , and  $R^{17}$  express a hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-12,  $-(CH_2)_m$ ,  $COOH$ , or  $-(CH_2)_mNH_2$ .  $m$  and  $n$  express the integer of 0-12.



<2> A tetracyano anthra quinodimethane compound expressed with said general formula (I) is an optical semiconductor electrode given in the above <1> which is a tetracyano anthra quinodimethane compound expressed with a following general formula (I-a).

General formula (I-a)

[0025]

[Formula 22]

[0026]In said general formula (I-a)Me expresses a methyl group. n expresses 0 or 1.

<3> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is at least one sort chosen from titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, nickel oxide, cobalt oxide and strontium titanate.

It has at least a connecting means which connects the electrode of the couple contacted to <4> electrolytes and the electrode of this couple so that energization is possible and at least one side of the electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.

<5> An electrode of a couple mutually connected so that energization was possible is contacted to an electrolyte. By irradiating at least one side of an electrode of this couple it is the photoelectric conversion method of producing a photoelectric conversion reaction and an electrode with which light is irradiated is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.

[0027]

[Embodiment of the Invention] (Optical semiconductor electrode) The optical semiconductor electrode of this invention has a photoelectric conversion layer by at least one sort chosen from the perylene compound expressed with the tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) on the surface of a metal oxide semiconductor.

[0028]- metal oxide semiconductor - As said metal oxide semiconductor there is no restriction in particular and it can choose suitably according to the purpose for example titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, strontium titanate etc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Especially in this invention the

reasons of a photoelectric transfer characteristic chemical stability manufacture ease etc. to titanium oxide is preferred also in these.

[0029] About the shape of said metal oxide semiconductor structure and a size there is no restriction in particular and it can choose suitably according to the purpose. For example as a structure of said metal oxide semiconductor It may be the structure which consists only of this metal oxide semiconductor and may be the structure in which the thin film layer of this metal oxide semiconductor was formed on conductive base material such as plate such as transparent electrode such as ITO glass and Nesa glass platinum copper and black lead or a mesh electrode.

[0030] - photoelectric conversion layer - The surface of said metal oxide semiconductor is adsorbed in at least one sort chosen from the perylene compound expressed with the tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) and said photoelectric conversion layer is formed in it.

General formula (I)

[0031]

[Formula 23]

[0032] In said general formula (I)  $R^1$  and  $R^2$  It may be mutually the same and may differ a hydrogen atom an alkyl group an aryl group an alkyl group an alkoxyalkyl group or an acyl group may be expressed and these may form the annular group of the following structure mutually. n expresses 0 or 1.

[0033]

[Formula 24]

General formula (II)

[Formula 25]

[0034] In said general formula (II)  $R^3$  and  $R^4$  Expressing the basis expressed with either following general formula (III) - (IX) these may be mutually the same it may differ and at least one side expresses the basis expressed with either following general formula (III) - (VII) and (IX). 1 expresses 0 - when it is a basis which expresses 0 when  $R^3$  and  $R^4$  are the bases expressed with either following general formula (III) - (VIII) and is expressed with following general formula (IX).

General formula (III)

[0035]

[Formula 26]

[0036] In said general formula (III)  $R^5$  and  $R^6$  may be mutually the same it may differ an aliphatic group an aromatic group or a heterocycle group is expressed and these may be replaced by a substituent.  $A^1$  expresses a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by a substituent.

General formula (IV)

[0037]

[Formula 27]

[0038] In said general formula (IV)  $A^2$  expresses a divalent aliphatic group aromatic group or heterocycle group and these may be replaced by the substituent.  $R^7$  and  $R^8$  may be mutually the same and it may differ a hydrogen atom a halogen atom the alkyl group of the carbon numbers 1-20- $(CH_2)_pCOOR^{18}$ - $(CH_2)_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$  is expressed.  $R^{18}R^{19}R^{20}$  and  $R^{21}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (V)

[0039]

[Formula 28]

[0040] In said general formula (V)  $A^3$  expresses a single bond or a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by the substituent.  $R^9$  expresses an aliphatic group an aromatic group or a heterocycle group and these may be replaced by the substituent.  $R^{10}$  A hydrogen atom a halogen atom the alkyl group of the carbon numbers 1-20- $(CH_2)_pCOOR^{18}$ - $(CH_2)_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}R^{19}R^{20}$  and  $R^{21}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20.  $p$  expresses the integer of 0-20.

General formula (VI)

[0041]

[Formula 29]

[0042] In said general formula (VI)  $A^4$  expresses a divalent aliphatic

grouparomatic groupor heterocycle groupand these may be replaced by the substituent. X expresses an oxygen atoma sulfur atomor  $>NR^{22}$ .  $R^{11}$  and  $R^{12}$  A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20- $(CH_2)_p$  Express  $_pCOOR^{18}-(CH_2)_pSO_3R^{19}$ or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}R^{19}R^{20}R^{21}$ and  $R^{22}$  express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VII)

[0043]

[Formula 30]

[0044]In said general formula (VII) $A^5$  expresses a single bond or a divalent aliphatic groupa aromatic groupor a heterocycle groupand these may be replaced by a substituent.  $R^{13}$  expresses a divalent aliphatic groupa aromatic groupor a heterocycle groupand these may be replaced by a substituent.  $R^{14}$  A hydrogen atoma halogen atoman alkyl group of the carbon numbers 1-20- $(CH_2)_p$  Express  $_pCOOR^{18}-(CH_2)_pSO_3R^{19}$ or  $-(CH_2)_pNR^{20}R^{21}$ .  $R^{18}R^{19}R^{20}$ and  $R^{21}$  express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.

General formula (VIII)

[0045]

[Formula 31]

[0046]In said general formula (VIII) $A^6$  expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. Y expresses  $-COOH-SOOH$ or  $-NH_2$ .

General formula (IX)

[0047]

[Formula 32]

[0048]In said general formula (IX)X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOVOaluminum (OH)Ga (OH)or In (OH).  $R^{15}R^{16}$ and  $R^{17}$  express a hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-12- $(CH_2)_mCOOHor -(CH_2)_mNH_2$ . m and n express the integer of 0-12.

[0049]As a desirable example of a tetracyano anthra quinodimethane compound expressed with said general formula (I)the following compound (I-1-30) is mentioned. The example in  $n=0$  was shown in Table 1and the example in  $n=1$  was shown in Table 2.

[0050]  
[Table 1]

[0051]  
[Table 2]

[0052] In this invention especially a tetracyano anthra quinodimethane compound that are points such as photoelectric conversion efficiency, an absorption wavelength region and an ease of manufacture and is expressed with a following general formula (I-a) also in these is preferred (compound expressed with said illustration compound (I-1)).  
General formula (I-a)

[0053]  
[Formula 33]

In said general formula (I-a) Me expresses a methyl group. n expresses 0 or 1.

[0054] A tetracyano anthra quinodimethane compound expressed with said general formula (I) For example it is compoundable by method to which the Anthraquinone derivative expressed with a following general formula (A) of a statement to JP63-104062A and malononitrile expressed with a following general formula (B) are made to reactor a method given in JP58-55450A etc.

[0055]  
[Formula 34]

[0056]  
[Formula 35]

[0057] Efficiently separation and since it is movable the tetracyano anthra quinodimethane compound expressed with said general formula (I) is efficient and can carry out spectral sensitization of the electric charge which it had an electronic receptiveness portion and an electron-donative portion and the absorption wavelength region is extended to the long wavelength region which is about 700 nm and was generated.

[0058] The following compound (II-1 - 13) is mentioned as a desirable

example of a perylene compound expressed with said general formula (II).

[0059]

[Formula 36]

[0060]

[Formula 37]

[0061]

[Formula 38]

[0062]

[Formula 39]

[0063]

[Formula 40]

[0064]

[Formula 41]

[0065]

[Formula 42]

[0066]

[Formula 43]

[0067]

[Formula 44]

[0068]

[Formula 45]

[0069]  
[Formula 46]

[0070]  
[Formula 47]

[0071]  
[Formula 48]

[0072]In this invention a following general formula (IX-a) is held as a perylene compound expressed with said general formula (II).

General formula (IX-a)

[0073]  
[Formula 49]

[0074]As a desirable example of a perylene compound expressed with said general formula (IX-a) the compound (IX-1 - 23) shown in Table 3 is mentioned.

[0075]  
[Table 3]

In Table 3  $H_2$  expresses two hydrogen atoms.

[0076]In the perylene compound which is said general formula (II) and is expressed  $R^3$  and  $R^4$  are the same. What is a basis expressed with either said general formula (III) - (IX) respectively is compoundable by for example making a 3,4,9,10-perylene tetracarboxylic anhydride and the compound expressed with following general formula (III') - (IX') respectively react.

[0077]  
[Formula 50]

[0078]  
[Formula 51]

[0079]  
[Formula 52]

[0080]  
[Formula 53]

[0081]  
[Formula 54]

[0082]  
[Formula 55]

[0083]  
[Formula 56]

[0084] In a perylene compound which is said general formula (II) and is expressed  $R^3$  differs from  $R^4$  mutually. What is a basis expressed with either said general formula (III) - (IX). For example, by making two sorts chosen from a 3,4,9,10-perylene tetracarboxylic anhydride and a compound expressed with said general formula (III') - (IX') react. Or it is compoundable by making two sorts chosen from a compound expressed with 3,4,9,10-perylene tetracarboxylic monoanhydride mono-metal salt and said general formula (III') - (IX') of a statement by United States patent 4th the No. 501 or 906 specification etc. react one by one.

[0085] A perylene compound expressed with said general formula (II) is excellent in chemical stability and endurance and is excellent in holdout in the surface of said metal oxide semiconductor and spectral sensitization can be carried out stably and efficient over a long period of time.

[0086] Formation of - photoelectric conversion layer - Said photoelectric conversion layer adds to a solvent at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I) and said (II). It can form in the surface of this metal oxide semiconductor easily by immersing said metal oxide semiconductor into a solution which dissolved this.

[0087] As said solvent profitably there is no restriction and it can choose



from publicly known solvents suitably according to the purpose. For example, amide system solvents such as ketone solvents such as alcoholic solvents such as methanol and isopropyl alcohol, acetone and methyl ethyl ketone, N,N-dimethylformamide and N-methyl pyrrolidone, water or these mixed solvents are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Also in the amide system solvents such as N,N-dimethylformamide are preferred. In this invention it is the purpose of raising solubility to said at least one sort chosen from a perylene compound expressed with a tetracyano anthraquinodimethane compound expressed with said general formula (I) and said (II) of solvents and acid and alkali etc. may be added in this solvent.

[0088] In order to promote adsorption to said at least one sort chosen from a perylene compound expressed with a tetracyano anthraquinodimethane compound which may perform said immersion at a room temperature and is expressed with said general formula (I) and said (II) of metal oxide semiconductors it may heat if needed.

[0089] After washing after said immersion using arbitrary solvents etc. by carrying out desiccation etc. An optical semiconductor electrode which has the photoelectric conversion layer by which at least one sort chosen from a perylene compound expressed with a tetracyano anthraquinodimethane compound expressed with said general formula (I) and said (II) was adsorbed and formed in the surface of said metal oxide semiconductor is obtained.

[0090] In a wide range of fields a semiconductor electrode of this invention can be used conveniently and can be used especially conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0091] (Photoelectric conversion device) A photoelectric conversion device of this invention may have at least a connecting means which connects an electrode of a couple contacted to an electrolyte and an electrode of this couple so that energization is possible and also may have a means of others suitably selected if needed.

[0092] Also in an electrode of said couple it is an optical semiconductor electrode of said this invention and another side is a counter electrode. As said counter electrode to oxidation and reduction if stable there will be no restriction in particular and according to the purpose it can choose from a publicly known thing suitably for example transparent electrodes such as plates such as platinum, gold and black lead, ITO glass and Nesa glass etc. are mentioned.

[0093] A wire, rod, plate, printed film or a vacuum evaporation film etc. which restriction in particular does not have as long as it has a

function in which an electrode of said couple can be connected as said connecting means so that energization is possible and consists of conductive material such as a publicly known lead or various metal carbon and a metallic oxide is mentioned. This connecting means is connected to an electrode of said couple so that energization is possible.

[0094] As said electrolyte there is no restriction in particular and it can choose suitably according to the purpose. For example, salt such as potassium chloride, a lithium chloride and tetraethylammonium perchlorate. A nonaqueous solvent solution such as acid such as alkali such as sodium hydroxide and potassium carbonate, sulfuric acid and chloride, these mixtures, these solution or these alcohol and propylene carbonate etc. are mentioned. In this invention it is the purpose such as attaining stabilization of the photoelectric current characteristic and a redox reagent which produces an oxidation-reduction reaction still more nearly reversibly [such as potassium iodide, iodine and p-benzoquinone] in said electrolyte may be added. A photoelectric conversion device of this invention can be used conveniently for a photoelectric conversion method of the following this inventions.

[0095] (A photoelectric conversion method) In a photoelectric conversion method of this invention an electrode of said couple mutually connected so that energization was possible is contacted to said electrolyte and a photoelectric conversion reaction is produced by irradiating at least one side of an electrode of this couple. [0096] In an electrode of said couple an electrode with which light is irradiated is an optical semiconductor electrode of said this invention and another side is said counter electrode.

[0097] - In a photoelectric conversion device and a photoelectric conversion method of photoelectric conversion reaction - this invention a photoelectric conversion reaction arises as follows. That is said optical semiconductor electrode and said counter electrode are first immersed into said electrolyte (solution). Next monochromatic light of at least one sort of absorption wavelength regions chosen as said optical semiconductor electrode from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I) and said general formula (II) Or an exposure of white light or multicolor light which includes one of the zones will transform such light energies into electrical energy.

[0098] According to a photoelectric conversion device and a photoelectric conversion method using a semiconductor electrode and this semiconductor electrode of this invention. Even if it irradiates with 300-700-nm

visible light as a light with which it irradiates especially good photoelectric conversion efficiency is acquired metal oxide semiconductor such as titanium oxide-- if independent it can use effectively to a wavelength band of visible light which cannot be used and luminous energy such as sunlight can be efficiently transformed into electrical energy.

[0099]

[Example] Hereafter although the example of this invention is described this invention is not limited to these examples at all.

[0100] (Example 1) 25 ml of alt. titanate acid tetraisopropyl was added gradually agitating violently in the mixed solution of 150 ml of pure water and the concentrated nitric acid 1.54g (specific gravity: 1.38). Temperature up was carried out to 80 °C continuing churning furthermore churning was continued at the temperature for 8 hours and the milky stable titanium oxide colloidal solution was prepared. This titanium oxide colloidal solution was condensed to 40 ml at 30 °C under decompression of 30mmHg. Said titanium oxide colloidal solution was coated with the spin coat method on the glass substrate (the following "ITO glass substrate" is called) with which the layer of ITO was covered and was calcinated at 500 °C for 1 hour. This operation was repeated 3 times and the titanium oxide layer about 1.0 micrometer thick was formed on the ITO glass substrate. When the crystal structure of the obtained titanium oxide membrane was checked with the X-ray diffraction method it was a mixture of an anatase and a rutile type. The ITO glass substrate which supported said titanium oxide layer was used as a metal oxide semiconductor.

[0101] After making the solution which dissolved in 50 ml of N,N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 °C for 12 hours this metal oxide semiconductor was washed in order of acetone and methanol and natural seasoning was carried out. By the above adsorption formation of the photoelectric conversion layer with said illustration compound (I-1) was carried out on the surface of said metallic-oxide N semiconductor.

[0102] Next the lead was connected to the layer portion of ITO covered by the glass substrate. The terminal area of said lead covered and adhered with the epoxy resin. The optical semiconductor electrode was produced by the above.

[0103] Drawing 1 is an approximate account figure for explaining the produced optical semiconductor electrode. The optical semiconductor electrode 1 has the layer 3 of ITO the titanium oxide layer 4 and the photoelectric conversion layer 5 with said illustration compound (I-1)

on the glass base material 2 at this order. The terminal area of the layer 3 of ITO and the lead 7 was covered with the epoxy resin as the adhesive agent 6 and has adhered with it.

In this terminal area the lead 7 is accommodated into the glass tube 8.

[0104] Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with said optical semiconductor electrode. Here saturated calomel electrode \*\* is immersed in a platinum electrode as the optical semiconductor electrode 1 and the counter electrode 9 which were produced and is immersed into the inside of the transparent glass cell 13 and the electrolytic solution 11 as the reference electrode 10. The electrolytic solutions 11 are 0.1M-sodium sulfate / 0.02M-potassium iodide solution. It is connected to the potentiostat 12 via the lead 7 as a connecting means and energization of each electrode is attained.

[0105] In this photoelectric conversion device it is held so that the potential of said optical semiconductor electrode 1 might be set to 0V to the reference electrode 10 and it is irradiated with white light (the xenon lamp of 500W illumination 4000lux) from the back side of the optical semiconductor electrode and the value of the photoelectric current at this time was measured with the potentiostat. The measurement result was shown in Table 4.

[0106] (Example 2) In Example 1 the outside which replaced the illustration compound (I-1) with the illustration compound (I-3) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 and enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 4.

[0107] (Example 3) In Example 1 the outside which replaced the illustration compound (I-1) with the illustration compound (I-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 and enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 4.

[0108] (Comparative example 1) In Example 1 the outside which did not use an illustration compound (I-1) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 and enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 4.

[0109] (Comparative example 2) The outside which replaced the illustration compound (I-1) with 2457-tetraiodofluorescein in Example 1

is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like the photoelectric conversion method was enforced and photoelectric current was measured. The measurement result was shown in Table 4.

[0110] (Comparative example 3) The outside which replaced the illustration compound (I-1) with copper (tetra KARUBOKI phthalocyaninato) (II) in Example 1 is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like the photoelectric conversion method was enforced and photoelectric current was measured. The measurement result was shown in Table 4.

[0111]

[Table 4]

[0112] (Example 4) In Example 1 a metal oxide semiconductor instead of making the solution which dissolved in 50 ml of N,N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 °C for 12 hours. The outside in which the solution which dissolved in 50 ml of 2% hydroxylation tetra (n-butyl) ammonium / ethanol solutions was made to immerse 50 mg of an illustration compound (II-4) at 70-80 °C for 1 hour produces an optical semiconductor electrode and a photoelectric conversion device like Example 1 and the photoelectric conversion method is enforced. Photoelectric current was measured. The measurement result was shown in Table 5.

[0113] (Example 5) In Example 4 the outside which replaced the illustration compound (II-4) with the illustration compound (II-9) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 5.

[0114] (Example 6) In Example 4 the outside which replaced the illustration compound (II-4) with the illustration compound (II-10) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 5.

[0115] (Comparative example 4) In Example 4 the outside which did not use an illustration compound (II-4) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4 enforced the photoelectric conversion method and measured photoelectric current.

The measurement result was shown in Table 5.

[0116] (Comparative example 5) In Example 4 the outside which replaced the illustration compound (II-4) with 2457-tetraiodofluorescein produced the optical semiconductor electrode and the photoelectric conversion device like Example 4 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 5.

[0117]

[Table 5]

[0118] (Example 7) In Example 1 a metal oxide semiconductor instead of making the solution which dissolved in 50 ml of N.N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 °C for 12 hours. The outside in which the solution which dissolved in 50 ml of N.N-dimethylformamide was made to immerse 100 mg of an illustration compound (IX-4) at 80-100 °C for 1 hour produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0119] (Example 8) In Example 7 the outside which replaced the illustration compound (IX-4) with the illustration compound (IX-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0120] (Example 9) In Example 7 the outside which replaced the illustration compound (IX-4) with the illustration compound (IX-9) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0121] (Comparative example 6) In Example 7 the outside which did not use an illustration compound (IX-4) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0122] (Comparative example 7) In Example 7 the outside which replaced the illustration compound (IX-4) with 2457-tetraiodo-3',4',5',6'-tetrachlorofluorescein. The optical semiconductor electrode and the photoelectric conversion device were produced like Example 7 the photoelectric conversion method was enforced and photoelectric current

was measured. The measurement result was shown in Table 6.

[0123] (Comparative example 8) In Example 7 the outside which replaced the illustration compound (IX-4) with copper (tetracarboxy phthalocyaninato) (II) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0124]

[Table 6]

[0125]

[Effect of the Invention] According to this invention available [ of the sunlight ] can be carried out efficiently it excels in photoelectric conversion efficiency stability endurance etc. and the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency can be provided using the optical semiconductor electrode which can be manufactured cheaply and easily and this optical semiconductor electrode.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is an approximate account figure of the optical semiconductor electrode of this invention.

[Drawing 2] Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with the optical semiconductor electrode of drawing 1.

[Drawing 3] Drawing 3 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 4.

[Drawing 4] Drawing 4 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 7.

[Description of Notations]

- 1 Optical semiconductor electrode
- 2 Glass substrate
- 3 The layer of ITO
- 4 Titanium oxide layer
- 5 Photoelectric conversion layer
- 6 Adhesive agent
- 7 Lead

- 8 Glass tube
  - 9 Counterelectrode
  - 10 Reference electrode
  - 11 Electrolytic solution
  - 12 Potentiostat
  - 13 Transparent glass cell
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